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NOVEL COMPOSITE MATERIALS: ALLOYS FROM IMMISCIBLE COMPONENTS

FINAL REPORT

June 17, 1988

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FINAL REPORT

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Period: April 1, 1987 - March 31, 1988

"Novel Composite Materials: Alloys from Immiscible Components"

Principal Investigator:

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List of manuscripts submitted or published under USARO sponsorship during the grant period:

1. Kirkor, E. W.; Michl, J. "Salted Iron Pentacarbonyl: Molecular Isolation in Alkali Halide Solids", submitted for

publication.

2. Kirkor, E. W.; Maloney, V. M.; Michl, J. "The Photochemistry of 'Salted' Quadricyclane and Norbornadiene: Alkali Halide Color Centers as Catalysts", submitted for publication.
3. Kirkor, E.; David, D.; Magnera, T.; Michl, J. "A Simple Method for the Production of Controlled Electroplated Designs on a Metal Surface", *Langmuir*, 1988, 4, 578.

Research Results

1. The ultrahigh-vacuum deposition chamber was transported to the University of Texas from the University of Utah. Damage caused by transportation was repaired. This unit permits deposition of solid matrices under clean conditions (base pressure of 10^{-9} Torr) onto a plate held at 20 K.
2. As hoped for, the use of a clean environment and of very low deposition temperatures *permitted us to accomplish the primary objective of the research, single molecule isolation of dopants in an alkali halide matrix*. Previously, we were only able to obtain alkali halide matrices containing aggregated dopants. This breakthrough opens new vistas in matrix isolation spectroscopy, photochemistry, and chemistry.
3. The evidence that the dopant molecules are truly individually isolated was obtained using $\text{Fe}(\text{CO})_5$. Upon irradiation, this molecule loses one or more CO fragments. If the sample is aggregated, the resulting primary product,

$\text{Fe}(\text{CO})_4$, adds immediately to a neighboring $\text{Fe}(\text{CO})_5$. The IR bands of the $\text{Fe}_2(\text{CO})_9$ product are characteristic and easily identified. This is the situation with samples deposited at excessive concentrations or at concentrations that are too high. With samples prepared under optimized conditions, no $\text{Fe}_2(\text{CO})_9$ is formed, only lower carbonyls of iron. Under certain conditions, we have detected the formation of the $\text{Fe}(\text{CO})_4\text{I}^-$ anion isolated in CsI. Its formation is attributed to the attack by an I^- anion from the lattice on the primary photofragment, $\text{Fe}(\text{CO})_4$. The by-product, CO, has also been identified by IR spectroscopy.

It is important to note that the deposition of $\text{Fe}(\text{CO})_5$ into an alkali halide matrix can be performed without thermal decomposition in spite of the thermal lability of this compound. This makes us optimistic concerning our ability to deposit fragile species intact.

These results were summarized in a full paper that has been submitted for publication (above ref. 1).

4. We have subsequently used the deposition conditions optimized for single molecule dopant isolation to investigate a chemical organic photochemical system, quadricyclane - norbornadiene. This investigation brought to light an interesting aspect of the use of alkali halides as matrix materials, namely their ability to support color centers.

Briefly, at temperatures where the H center, most easily thought of as an $\text{I}_2^{\cdot -}$ defect, is immobile, UV irradiation

tion of alkali-halide matrix isolated norbornadiene yields quadricyclane in a fashion familiar from solution photochemistry. However, at higher temperatures, where the H centers are mobile, the UV photoprocess occurs in the opposite sense and quadricyclane yields norbornadiene. We have proposed that a photogenerated H center acts as a catalyst. Its oxidizing power is sufficient to convert quadricyclane into its radical cation, which opens to the norbornadiene radical cation, which in turn is a sufficiently strong oxidant to regenerate the H center and yield norbornadiene.

We have found that even the UV irradiation of a suspension of powdered CsI in a solution containing quadricyclane effects its ring opening to norbornadiene, presumably by a similar mechanism occurring on the surface of the microcrystals.

These results have been written up in a full paper and submitted for publication (above ref. 2)

5. In research directed along somewhat different lines, we have utilized the vacuum equipment available to us from this project to demonstrate the feasibility of a novel idea for monomolecular layer photoimaging. We have demonstrated the formation of both positive and negative images of a laser beam pattern on a platinum surface. The beam causes desorption of a monomolecular layer of either CO or iodine in the irradiated area. When the desorption is performed in

the atmosphere of the other partner, either iodine or CO, the freed-up areas are immediately filled and one ends up with a stable image recorded either as islands of iodine in a sea of a CO-covered surface or islands of CO in a sea of an iodine-covered surface. Development is performed by electrodeposition of a thin layer of silver under conditions where it deposits only on the iodine-covered but not on the CO-covered areas.

These results were published as a full paper in above ref. 3.

Josef Michl May 27, 88
Josef Michl Date